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THE CHEMISTRY OF MATERIALS UNDER EXTREME ENVIRONMENTAL
CONDITIONS

W. F. Libby

California University

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FINAL REPORT OF A FIVE YEAR PROGRAM

OF

"AFOSR PROGRAM AT UCLA IN THE CHEMISTRY OF
MATERIALS UNDER EXTREME ENVIRONMENTAL CONDITIONS"

by

W. F. LIBBY

DEPARTMENT OF CHEMISTRY

AND

INSTITUTE OF GEOPHYSICS AND PLANETARY PHYSICS

UNIVERSITY OF CALIFORNIA

LOS ANGELES

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Principal Investigator

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) During the last four years there have been about six major projects in the area of interest to the energy and environment, and the space program. Beginning with the energy and environment, the principle effort has been to develop a non-noble metal auto exhaust catalyst. This effort began with the observation that there were certain evidences that the rare earth cobalt perovskites, LaCoO_3, had catalytic properties strongly indicating that they might take care of the auto exhaust problem, at		

20. Abstract (continued)

least in removing unburned hydrocarbons and carbon monoxide. This and the strong possibility that they would not be subject to lead poisoning and would not require noble metals led to our mounting a substantial effort which shows substantial promise of success.

In the space chemistry area we have helped develop an understanding of Venus and the Earth atmospheres. Venus could not precipitate limestone because there was no place where it could freeze water, break rock and so liberate calcium for limestone precipitation. The water gas reaction produced CO_2 and hydrogen from primeval organic matter fired by the radioactive heat of the newly formed planet, the hot steam forming CO_2 and hydrogen. The hydrogen escaped from the planet. Presumably on Earth this same thing happened but on Venus the CO_2 accumulated in the atmosphere to some 90 atmospheres (terrestrial measure). On the Earth it formed limestone and fossil organic deposits. The amount of water consumed in this gigantic effort was about one kilometer in depth. Thus, we predict that there are oceans on Venus at the poles, since it appears most unlikely that all the water was consumed in the reaction.

On Jupiter our work has been on the thesis that the strong radio signals are caused by electron spin resonance emissions from organic radicals in the reducing atmosphere. The strong planetary magnetic field (some 10 gauss at the poles) would give the observed frequencies. It is only fair to say that our thesis has not been universally accepted but there seems to be no other explanation for the richness of the radio signals and the coincidence with likely free radicals.

Other broad general interests in our program have been high pressure chemistry. We have been mainly concerned in the last four years with trying to understand the effects of high pressures above 10,000 atmospheres on organic and biochemical reactions. We appear to have found that the dimerization of anthracene has a negative temperature coefficient under pressures of 5,000 atmospheres. We have been pursuing the effects of pressure on important enzymes and the growth of bone. These results are most suggestive and exciting. Our most recent Ph.D. graduate, Randy Murphy, is becoming a post-doctoral working with Dr. Marshall Urist, M.D. of UCLA medical school, who has discovered a bone growing enzyme which promises to be of great importance to bone surgery.

In our concern about the energy matters we have concentrated on the discovery of oil and other resources buried in the sedimentary deposits.

In the chemistry of ionized matter we have found that singlet oxygen can be involved in the radiolysis of water.

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SENIOR RESEARCH PERSONNEL

Rainer Berger

Howard Katzman

Paul Corneil

Leona Libby

E. E. Ferguson

Paul Calvin Maybury

N. Fukuta

Joseph Seckbach

Abdolah Herdifer

George Zimmerman

JUNIOR RESEARCH PERSONNEL

Saulius Alkaitis

John Marshall

Dale Barry

J. Moss

Mitchell Cooper

Randy Murphy

Edward Greer

Louis Pandolfi

Sim Hoffman

Pat Payton

John Kerridge

Lee Pedersen

Joel Leventhal

Mike Sheridan

Jeff London

Saburo Yashita

Summary

The Air Force Office of Scientific Research over the years has supported our efforts most generously. It has been most kind in its tolerance of our wide range of objectives. It supported the development of radiocarbon dating and its applications to archaeology and geoscience and the discovery of natural tritium and its application to hydrology and meteorology and geophysics as well as the core work in chemistry.

During the last four years there have been about six major projects in the area of interest to the energy and environment, and the space program. Beginning with the energy and environment, the principle effort has been to develop a non-noble metal auto exhaust catalyst. This effort began with the observation that there were certain evidences that the rare earth cobalt perovskites, LaCoO_3 , had properties strongly indicating that they would take care of the auto exhaust problem, at least in removing unburned hydrocarbons and carbon monoxide. This and the strong possibility that they would not be subject to lead poisoning and would not require noble metals led to our mounting a substantial effort. It now has gone the course of our organizing an independent company to develop the catalyst under contract with Du Pont de Nemours Company. We are well down the road of testing and proving (Promising Catalyst for Auto Exhaust. W. F. Libby. Science 171, 499-[1971], Unseparated Rare Earth Cobalt Oxides as Auto Exhaust Catalysts. Lee Pedersen and W. F. Libby. Science 176, 1355-[1972]).

In addition to the development of the rare earth perovskites for auto exhaust catalysts, the effort titilated the petroleum companies to further examine non-noble metal catalysts for their own use in modern refineries. A long time ago, base metal catalysts were standard in the refinery. It looks like they may be returning. The knowledge of solid state physics which has been gained in recent years had led to the application of perovskites to the fuel cell and auto exhaust catalyst problems. They appear to have opened a new door in the area of heterogeneous catalysis.

In the space chemistry area we have helped develop an understanding of Venus and the Earth atmospheres. Venus could not precipitate limestone because there was no place where it could freeze water, break rock and so liberate calcium for limestone precipitation. The water gas reaction produced CO_2 and hydrogen from primeval organic matter fired by the radioactive heat of the newly formed planet, the hot steam forming CO_2 and hydrogen. The hydrogen escaped from the planet. Presumably on Earth this same thing happened but on Venus the CO_2 accumulated in the atmosphere to some 90 atmospheres (terrestrial measure)². On the Earth it formed limestone and fossil organic deposits. The amount of water consumed in this gigantic effort was about one kilometer in depth. On the Earth limestone formed together with organic matter from plants and it is clear that a colossal amount of water was required to accomplish all of this. Thus we predict that there are oceans on Venus at the poles. It seems unlikely that the Venus water would be titrated for the exact amount required to make 90 atmospheres of carbon dioxide with no water left over and there seems to be no escape mechanism for water on Venus

any more than there is on the Earth. It is very intriguing to try to understand if polar oceans on Venus do exist what the possibilities of life in them are. We did experiments on high pressure CO_2 saturated warm water solution and found that algae from the Yellowstone hot springs and other places did grow. We have strongly suggested to NASA that polar flybys be made over Venus with radar sounders to detect flat surfaces at the poles (Vegetative Life on Venus? Or Investigations with Algae which Grow Under Pure CO_2 in Hot Acid Media and Elevated Pressures. Joseph Seckbach and W. F. Libby. Space Life Science 2, 121-[1970] and also published in Planetary Atmospheres. Edited by Sagan et al., 62-[1971]).

On Jupiter our work has been on the thesis that the strong radio signals are caused by electron spin resonance emissions from organic radicals in the reducing environment. The strong planetary magnetic field of some 10 gauss at the poles would give the correct frequencies. It is only fair to say that our thesis has not been universally accepted but there seems to be no other explanation for the richness of the radio signals and the coincidence with likely free radicals in the strength of the Jupiter field. Arrangements have been made with the University of South Florida (Professor Sylvan Bloch) for laboratory experiments and further work is planned at UCLA (Stimulation of Jupiter's Radio Emission by Io. L. Marshall and W. F. Libby. Nature 214, 126-[1967], Radio Reflection by Free Radicals in Earth's Atmosphere. J. D. Barry, Paul J. Coleman, W. F. Libby, and L. M. Libby. Science 156, 1730-[1967], Life on Jupiter? W. F. Libby. Origins of Life 5, 483-[1974]).

Analysis of the isotopic composition of the carbon in meteorites particularly the carbonaceous chondrites seems to indicate (despite wild fluctuations the origin of which is unknown and which applies to most of the elements including oxygen) that there is a general kind of average around the composition of the Murchison meteorite organic matter of some 7 per mille light in the $\text{C}^{13}/\text{C}^{12}$ ratio relative to the PDB standard. The Murchison organic matter has been proven by amino acid analysis to be non-biogenic and therefore not contaminated. The Murchison meteorite averages at an isotopic carbon composition which compared with the composition of limestone and fossil fuels indicates that the Earth has 2/3 of its carbon in limestone and 1/3 in fossil fuels. Now considering this in view of the 90 atmospheres of CO_2 on Venus, we deduce that the amount of sedimentary limestone and dolomite is substantially larger in total than that now recorded in the geochemical literature. This is understandable in view of the current theories of continental drift, the motion of the ocean floor, and the turnover of the seabed taking sediments down into the mantle. Most exciting is the possibility that there are enormous deposits of fossil fuel as yet undiscovered. This we consider a potentially important contribution in the area of the energy program which strongly urges expanding our exploration efforts. (Terrestrial and Meteorite Carbon Appear to Have the Same Isotopic Composition. W. F. Libby. Proceedings of the National Academy of Sciences 68, No. 2, 377-[1971]).

Other broad general interests in our program have been high pressure chemistry. We have been mainly concerned in the last four years with trying to understand the effects of high pressures above 10,000 atmospheres on organic chemical reactions. There is an abundant literature due to many people such as Dr. Cheves Walling, in the range of pressures

between 5,000 and 10,000 atmospheres which is of enormous interest. We have in fact in the last two or three years investigated the matter of the effect of such pressures on globular proteins but our most interesting findings are that we have a reaction in anthracene which proceeds at liquid nitrogen temperatures at pressures of 60,000 kilobars at speeds higher than those at 20°C and 1 atmosphere. The second point is that we have found that the irradiation of solid anthracene with Co^{60} gamma rays increases the high pressure reactions at liquid nitrogen temperatures by a factor of 10 or more. Most of the products are dimers of anthracene. At higher temperatures the products include fragmentation products.

We have been pursuing the effects of pressure on important enzymes and the growth of bone. These results are most suggestive and exciting. Our most recent Ph.D. graduate Randy Murphy is becoming a post-doctoral working with Dr. Marshall Urist, M.D. of UCLA medical school, who has discovered a bone growing enzyme which promises to be of great importance to bone surgery. He will proceed to research the chemical physics of the bone growing enzymes. Our present indications are that the enzyme is entirely different from hemoglobin and other globular proteins for the denaturation reaction under pressure in that it is much more resistant with a considerable tolerance to high pressures.

We have continued our long time interest in electron tunnelling in chemistry. Dr. Britton Chance and co-workers of the Johnson Foundation have given evidence that tunnelling is important in the cyclochrome-c oxidation reduction catalysis. It is becoming clear now that the basic thesis that electron tunnelling is important may be correct and that much of electrochemical phenomenology is due to the fact that electrons do tunnel through films at the electrodes. We have studied the kinetics of the dissolving of CrCl_3 in water interpreting it as an electron tunnelling transfer phenomenon. Our most recent accomplishment in this area has been in radiation chemistry. It appears that tunnelling may be important in the efficient conversion of sunlight for the promotion of oxidation reduction reactions. Micelles negatively charged appear to promote photo-ionization and the production of aquated electrons. This may be an enormously important finding and have great potential in the energy field. (The actual work was done in Berlin by Dr. Alkaitis). (The Chemical Impact of the Franck-Condon Principle and of Electron Tunnelling. W. F. Libby. Topics in Modern Physics - A Tribute to Edward U. Condon. Edited by W. E. Brittin and H. Odabasi. Colorado Associated University Press, Boulder, Colorado [1971], Catalyzed and Uncatalyzed Dissolution of Anhydrous Chromic Chloride in Aqueous Solutions. A. Hendifar, W. F. Libby, and George Zimmerman. The Journal of Physical Chemistry 78, 1993-[1974]).

We have been broadly concerned with environmental matters and have created a new doctoral degree for professionals trained to make environmental assessments in a judicious and objective manner with a broadly based graduate education and training to treat actual assessment problems more or less as a medical doctor treats human illness objectively and sympathetically allowing the patient to make the decision. We have fifty graduate students in the new program which now has been fully authorized by the University of California.

In addition to the new teaching program, there is an extensive program on research in the environmental area, in particular we were involved in the CIAP program in the Department of Transportation on the potential impact of the super sonic transport aircraft on the stratosphere. Our former student, Allen Grobecker became director of this program and we believe it constitutes one of the highlights of the U. S. technological achievement in the last decade.

In our concern about energy matters we have concentrated on the discovery of oil and other resources buried in the sedimentary deposits. There appears to be a remarkable correlation with the heat flow patterns high heat flows with the richness of the deposits following (Geographical Coincidence of High Heat Flow, High Seismicity, and Upwelling, with Hydrocarbon Deposits, Phosphorites, Evaporites, and Uranium Ores. W. F. Libby and L. M. Libby. Proceedings of the National Academy of Sciences 71, 3931-[1974])).

1. Auto Exhaust Catalysts (Promising Catalyst for Auto Exhaust. W. F. Libby. Science 171, 499[1971], Unseparated Rare Earth Cobalt Oxides as Auto Exhaust Catalysts. Lee A. Pedersen and W. F. Libby. Science 176, 1355[1972], Auto Exhaust Catalysts. W. F. Libby. Annals of the New York Academy of Sciences 213, 243-[1973], Hydrocarbon Emissions from Jet Engines Operated at Simulated High Altitude Supersonic Flight Conditions. Howard Katzman and W. F. Libby. Preprint Volume, 2nd International Conference on the Environmental Impact of Aerospace Operations in the High Atmosphere, July 8-10, 1974).

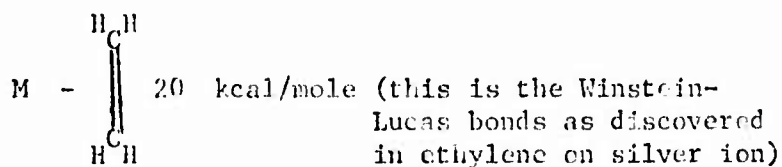
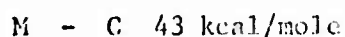
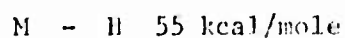
The observation that non-noble metal oxides could rival platinum for the fuel cell electrodes (D. B. Meadowcroft. Nature 236, 847-[1970]) led us to suggest that the rare earth cobalt oxides such as LaCoO_3 could be used as auto exhaust catalysts. Research on this idea has proven quite promising and the present indications are that there is a good chance for a non-platinum catalyst which would be tolerant of lead in gasoline with the consequence that the lost mileage due to the removal of lead from gasoline as required by the present platinum catalyst could be recovered. Also there is the further consequence that we need be dependent no longer on foreign sources to such a critical degree as we are in the case of platinum catalysts. The general situation is that we are in the process of testing the catalyst in collaboration with the Du Pont company determining the actual behavior on cars. Certain worries remain. The question of thermal instability for the substituted perovskites is german. The substituted perovskites have superior activity (the strontium substituted with 20 atom percent of the lanthanum replaced by strontium or some other divalent element have some thirty-fold greater activity both for the oxygen electrode in the fuel cell and in the oxidation of hydrocarbons and carbon monoxide. Our group has fostered the unsubstituted perovskites because of their proven thermal stability and

resistance to such temperature excursions as backfires.

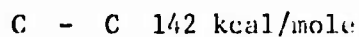
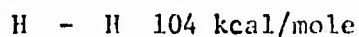
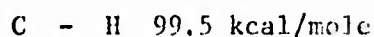
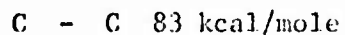
The fundamental principles of heterogeneous catalysis are becoming clearer slowly. We have contributed by conducting a survey of metallic oxides both natural minerals and synthetic compounds. Our conclusions are:

1. The oxides most catalytically active are those of the transition elements. Certain strongly acidic aluminosilicates can exhibit some activity.
2. The common mineral hematite Fe_2O_3 is a good catalyst and this property may have played a substantial role in geochemistry. The deposition of manganese nodules consisting mainly of Fe_2O_3 and MnO_2 are possibly controlled in their deposition by this property. The dissolved oxygen in sea water appears to oxidize both ferrous Fe^{++} and manganous Mn^{++} ions on the Fe_2O_3 surface causing the deposition of the insoluble Fe_2O_3 and MnO_2 oxides. The most of the nodules are roughly spherical in shape and lie on the bottom like billiard balls on a table not protruding into the sediments to any substantial degree. This strange circumstance has been explained as being due to the absence of oxygen in most of the sediments and the voracious attack of the bacterial organisms on higher valent oxides Fe_2O_3 and MnO_2 in lieu of oxygen reducing them to the soluble ions Fe^{++} and Mn^{++} which then are carried up into the sea water. Thus penetration of the growing nodule into the bottom sediments is prevented.

3. The catalytic properties of the transition element compounds appear to be due to the d orbitals which can form several bonds simultaneously on a single atom, bonds which are not too strong to be broken and yet are strong enough to dissociate ordinary s p bonds. A typical set of bond energies which seems to apply to essentially all of the transition element is:



The bond strengths appear to apply to most of the transition elements. Thus, the hydrogenation of ethylene can be envisaged as follows, recalling that:



Step I: Addition of H_2 to M



Step II: Addition of C_2H_4



Step III: Convert to two bound methyl groups

$\text{H}_3\text{C} - \text{M} - \text{CH}_3$	-	+
	43	55
	43	55
	99.5	20
	<u>99.5</u>	<u>147</u>
	-285	277

$$\Delta H = -8$$

Step IV: Form ethane gas

$$\Delta H = 43 - 83$$

$$\begin{array}{r} 43 \\ \hline +3 \end{array}$$

It seems very likely from the heterogeneous catalyst literature that all compounds of the transition elements as well as the elements themselves are active.

The perovskite crystals which have had our main attention is proving to be attractive for many catalytic tasks and may be opening a new chapter in oil and coal refining.

II. Plasma Chemistry (Radiation Chemistry) (Mechanism for the Fixation of Nitrogen by Lightning. E. E. Ferguson and W. F. Libby. *Nature* 229, 37-[1971], Possible Formation of Singlet Oxygen in the Radiolysis of Water Under High Pressure Oxygen. S. A. Alkaitis and W. F. Libby. *Nature Physical Science* 244, 143-[1973], and Polymer Production in the γ Radiolysis of Methane, Ethane, and Ethylene Solutions in Liquid Argon. M. E. Sheridan, E. Greer, and W. F. Libby. *J. Amer. Chem. Soc.* 94, 2614-[1972])).

The dramatic effects of ionizing radiation in promoting chemical reactions have been known for many years. In our laboratory we have concentrated on setting a body of principles generally applicable using data obtained on hydrocarbons in condensed systems at low temperatures. During the last four years, we have made essentially three contributions:

(1) The mechanism for the fixation of nitrogen by lightning which turns on the low ionization potential of nitric oxide produced by the extreme temperature produced by the bolt. The NO^+ so formed reacts with water to form nitrous acid HNO_2 which is water soluble and falls in the rain of the thunderstorm. (2) Further details on the polymer production from the gamma radiolysis of methane and other light hydrocarbons dissolved in liquid argon. We find that the gamma rays ionize the argon solvent since it is heavier and more abundant but that the effect on the solvent methane as though it were preferentially attached. This we interpret as being due to electron transfer by a tunnelling process from the solute methane, ethane, or ethylene to the ionized argon resulting in the formation of the hydrocarbon ion which then proceeds to react. Our present understanding of the reactions is not complete but the picture is becoming clearer. We produce a series of polymers of methane beginning with ethane and then a series of higher hydrocarbons in the range of 10 to 18 carbons and culminating in a $\text{C}_{20}\text{H}_{40}$ polymer at yields about half of the total methane destroyed, i.e., half ethane and half higher hydrocarbon. With ethane as the solute the yields are almost exactly doubled than from methane as though the half that went to ethane when methane was used now contributes to the heavy hydrocarbons. These are intriguing observations. We move now at this stage of the research to Mitchell Cooper undertaking his doctoral thesis using isotopic tracers to determine the detailed mechanism. At present it seems we are dealing with the carbonium ions CH_3^+ , C_2H_5^+ etc., which attack to form higher carbonium ions and release H_2 . Of course neutralization finally occurs. The question of how they can grow to the magnitude

observed is most intriguing.

The gamma radiolysis of water is a subject of very great importance in atomic power and in radiobiology. We have investigated the effects of high pressure oxygen on the radiolysis of aqueous ferrous sulfate solution to produce ferric sulfate in sulfuric acid solution and have found that there is an effect which apparently is due to the generation of singlet oxygen molecules produced by the gamma rays. The reality of the result was checked in separate experiments with generated singlet oxygen.

Our general work on electron tunnelling and plasma chemistry utilizing argon and xenon solvents with higher ionization potentials than the solute hydrocarbons begins to fit together in a kind of general picture. Early work principally by Burton and co-workers had shown that in solutions of benzene and cyclohexane the benzene plays a commanding role in reducing the overall sensitivity of the solutions to ionizing radiation. Our work on hydrocarbon solutions in xenon and argon was undertaken with this principle in mind since both xenon and argon have higher ionization potentials than the hydrocarbons. The very definite effect of essentially total transfer down to concentrations of a fraction of one mole percent strongly suggests electron tunneling. The high effect in yields of product in the ratio of the concentration of the solvent to solute suggests that if we ever discover important products from gamma radiology this principle might be of considerable importance in reducing costs.

In radiobiology it appears that the principle may be of importance. Among the vital molecules in living systems there are a number of aromatic systems and it seems to be likely that the ability of the aromatic

systems to resist ionizing radiation and to protect neighboring non-aromatics may be important in biophysics.

- III. High Pressure Inorganic Chemistry (Sintered Diamond Compacts with a Cobalt Binder. H. Katzman and W. F. Libby. *Science* 172, 1132-[1972], One-Parameter Equation of State for Metals and Certain Other Solids. L. M. Libby and W. F. Libby. *Proc. Nat. Acad. Sci.* 69, 3305-[1972])

Our efforts to produce a useful cutting tool from sintered diamond compacts with cobalt binder are arrested because there are no funds for producing the samples needed for testing. There seems to be little doubt that a tool in which the diamond crystals are small and randomly oriented and firmly, possibly chemically bonded to the cobalt should be superior. We have had many requests for samples to test. It could be important to produce such samples for the machine tool industry.

Our studies of the compressibilities of both metals and non metals have indicated that there are certain general relations of considerable potential usefulness that could be vitally important to understanding the interior of the planets, particularly Earth. Understanding of the properties of materials as subjected to the pressures and stresses in normal operations such as in machines took work and destructive testing and catastrophic failure could be very important. It may be that the empirical equations we have derived are more or less equivalent to those of other equations of state but ours have an appealing simplicity and ease of use.

- IV. Radiation Damage in Crystals (Non-Etching Optical Detection of Fission Tracks Using Teflon. P. C. Maybury and W. F. Libby. *Nature* 254, 209-[1975]).

For many years the Principle Investigator was deeply involved in Hot Atom Chemistry, i.e., the chemical effects of atoms having undergone

nuclear transmission. Of course, all of the atoms affected by nuclear transmission are in this category. Among those most affected are the fission products since their energies are so enormous. In recent years, there has been a breakthrough discovery by Price, Walker, and Fleischer of a new dating technique using the damage by fission products in minerals containing uranium impurities. It has been shown that these tracks can be etched to visible size using suitable etching techniques, filled with ink and measured and counted with optical microscopes.

During the last two years we have undertaken an effort to develop an additional approach, namely a non-etching development technique so the true size and shape of the tracks might be discovered with the electron microscope. The first step was to achieve optical detection. We chose a solid which was essentially non-etchable, namely Polytetrafluorethylene. We irradiated it with fission products from a Californium²⁵² source and approached the matter of developing the bundle of free radicals which in our mind is likely to form by the recoiling particle of some 100 Mev energy by reacting it with acrylic acid to bind the olefinic acid to the free radicals and in a second step adding a fluorescent dye Rhodamine B to bind the acidic carbonyl to the basic Rhodamine B. Following this, we exposed to ultraviolet light and observed fluorescence in the visible with a high-powered optical microscope. A filter was used to exclude the ultraviolet light. The irradiated sample was scintillating and tracks were clearly visible and photographs were taken.

It would seem that a follow-up research would show that binding the free radicals with a lead or heavy metal containing olefinic compound might

give an image that could be photographed by the electron microscope. This could reveal the lengths and diameters and perhaps other interesting features of the damage column - the unetched fission track.

- V. Electron Tunneling in Chemistry (Theory of Electron Exchange Reactions in Aqueous Solution. W. F. Libby. J. Phy. Chem. 56, 864-[1952], Electron Transfer Among The Transition Elements. The Controlling Role of the Franck-Condon Principle on Rates. W. F. Libby. J. Chem. Phys. 38, 420-[1962], The Chemical Impact of the Franck-Condon Principle and of Electron Tunneling. W. F. Libby. Topics in Modern Physics - A Tribute to Edward U. Condon. Edited by W. E. Brittin and H. Odabasi, Colorado Associated University Press, Boulder, Colorado [1971], Catalyzed and Uncatalyzed Dissolution of Anhydrous Chromic Chloride in Aqueous Solutions. A. Hendifar, W. F. Libby and George Zimmerman. The Journal of Physical Chemistry 78, 1993-[1974]).

Early in the report period the Principle Investigator wrote a general review on the role of electron tunneling in chemistry and the importance of the electronic Franck-Condon principle as a consequence. The general review article dealt with the early work of Mott on the oxidation of aluminum and of the Principle Investigator on the electron transfer exchange between the inorganic ions, manganate and permanganate, followed by the realization in 1952 that the speed of tunneling transfer invoked an electronic Franck-Condon principle which requires that both the receptor and donor molecules be in closely similar geometry before the electron can transfer. This very broad principle has over the years seemed to us to have great potential in chemical kinetics. During the last period of this recent grant, further investigation was undertaken. Following along with observations of Taube we have studied the anomalously slow rate of dissolving of chromic chloride CrCl_3 in aqueous solutions and the catalysis of this rate by chromous ion Cr^{++} . Although details remain to be elucidated and some question remains about the mechanism it seems very likely that the essential and rate determining process is the transfer of

an electron from the catalytic chromous ion next to the crystalline surface to produce surface bound chromous ion and of course chromic ion in solution. The stringencies of the transfer from the electronic Franck-Condon may account for most of the detailed observations.

IV. High Pressure Organic Chemistry (Ph.D. thesis, "Effects of High Pressure on Organic and Biological Systems", by Randall Murphy)

We find that very high pressures have effects on organic materials which are different from temperature effects. Reactions can be made to occur at liquid nitrogen temperatures at 60,000 atmospheres and above which do not occur, or only to a much smaller extent, at room temperature and the same pressures. In some ways these low temperatures yield less complex products than do the temperature induced reactions at low pressures. Most of our data have to do with anthracene and the production of its dimers. It seems definitely clear that the dimerization of this aromatic molecule is best promoted by high pressure at temperatures approximately 77°K. The presence of cations and trapped electrons induced by Co⁶⁰ gamma radiation further facilitates the reactions.

Studies of hemoglobin under pressure have shown us a number of details about the denaturation process for globular proteins, which are illuminating the work done earlier both in our laboratory and elsewhere and leads us to suggest that high pressure has considerable promise in biophysics and biochemistry. As a result we have affiliated with Dr. Marshall Urist who has discovered a bone growing enzyme and bone collagen and have been experimenting on the effects of pressures in the vicinity of 5,000 bars on this enzyme and the other constituents of the complex biological system which leads to the deposition of bone. Randy Murphy plans to do postdoctoral work for Dr. Urist on this general subject.